RÔLE OF JAHN-TELLER EFFECT IN THE LIGAND FIELD THEORY OF COPPER FLUOSILICATE HEXAHYDRATE

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ABSTRACT. The magnetic anisotropy and susceptibility of $CuSiF_6.6H_2O$ have been measured in the temperature range 90°–300° K. The crystal is found to undergo a phase change below ~285°K showing an anomalous anisotropy behaviour. The theory for the susceptibility of $Cu^{2+}(H_2O)_6$ cluster has been worked out based on an approximate Jahn-Teller model, taking into account the effect of the trigonal field which gives rise to a slight anisotropy in the g-values in the above temperature range.

INTRODUCTION

The optical and e.s.r. spectra of the hexahydrated copper-fluosilicate have received considerable attention in recent years, although no magnetic susceptibility data have as yet been published. The crystal belongs to the trigonal (rhombohedral) system with $\alpha = 111.5°$ (Groth, 1906) and is believed to be isomorphous with the similar ferrous salt, the detailed structure of which has been worked out by Hamilton (1962). There is one molecule in the unit cell, each Cu^{2+} ion being octahedrally coordinated to six water molecules, slightly elongated along the three-fold axis of the octahedron which coincides with the trigonal axis of the crystal so that the crystalline magnetic data can be directly correlated to ionic values.

The octahedrally coordinated copper complexes, $Cu^{2+}Y_6$, exhibit an interesting configurational instability of the Jahn-Teller type when the ligand field surrounding the Cu^{2+} ions is predominantly cubic with a weak trigonal component. This effect has been pointed out by Van Vleck (1939), and has been discussed in more details by a number of other workers (Öpik and Pryce, 1957; Moffitt and Liehr, 1957; Moffitt and Thorson, 1957; Liehr and Ballhausen, 1958; Mary O' Brien, 1964; and Pryce, Sinha and Tanabe, 1965). The effect has been observed in the e.s.r. spectrum by Bleaney and Ingram (1950),. Bijl and Rose-Innes (1955) and

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Bleaney, Bowers and Trenam (1955). Abragam and Pryce (1950) were the first to introduce the idea of the dynamic Jahn-Teller effect in copper complexes, and showed that the g-values and hyperfine structure constants in copper salts with trigonal symmetry should remain appreciably istropic except at very low temperatures. The isotropy of the g-values between 90° and 300°K has been observed by Bleaney and Ingram (1950) and by Yokozawa (1954) but no data at hydrogen and helium temperatures are available. Bleaney and Bowers (1952) also observed that the e.s.r. spectrum changes as the temperature is lowered to 60°K. O'Brien (1964) has discussed the isotropy of g-values of the octahedrally coordinated d^9 ions at high and low temperatures, in which the Jahn-Teller term is taken linear in the normal coordinates, Q. Liehr and Ballhausen (1958) included the terms of higher order in Q and obtained anisotropy of g-values at low temperatures, but their calculation was based on a purely electrostatic model and no account was taken of the covalency effect between the central paramagnetic ion and the ligands. The present paper deals with the theory of magnetic anisotropy and susceptibility of hexahydrated copper fluosilicate in which the Cu^{2+} ion is in a field of trigonal symmetry, in the range 300° to 90°K. The covalency between the central ion and the ligands as well as the additional quadratic terms in the normal coordinates have been included. Attempts have been made to fit this theory with the experimental results on magnetic anisotropy and the mean susceptibility of $CuSiF_6$. $6H_6O$ measured between 300°K and 90°K by Majumdar (1966) in this laboratory, consistently with the available optical absorption results (Pappalardo, 1961) and the paramagnetic resonance data of Bleaney and Ingram (1950) and Yokozawa (1954).

EXPERIMENT

(a) *Preparation of the crystal*

Copper fluosilicate was prepared by dissolving stoichiometric proportions o copper carbonate (basic) and precipitated silica in 38% hydrofluoric acid and crystallizing on a water bath. It was recrystallized from a nearly saturated slightly acid aqueous solution for further purification. It may be mentioned here that a tetrahydrated fluosilicate of copper (monoclinic) is also reported to be formed from aqueous solutions under certain conditions and there is some confusion in the literature regarding the formation of these two crystals. Groth (1906) states that the hexahydrate crystallizes at ordinary temperatures while Bleaney and Ingram (1950) state that the undiluted hexahydrate is not formed from aqueous solutions, the tetrahydrate crystallizing instead. Yokozawa (1954) and Ohtsuka (1965) mention that the hexahydrate crystallizes below 30°C while Pappalardo (1961) states that the tetrahydrate is generally formed at room temperature, (*sic*) although the hexahydrate is also sometimes formed. Evidently, the exact condi-

tions of formation of these crystals are quite critical and need to be determined precisely. In the present experiments it was found that

(i) only the hexahydrate is obtained in the temperature range 5°~15°C;

(ii) at or above 30°C only the tetrahydrate crystallizes, and

(iii) in the low temperature range (5°—15°), the last crop of crystals sometimes contain both tetra and hexahydrates. Very probably the percentage of the constituents in solution may have a decided effect in modifying the range of stability of the two phases below~30°C, which may explain the conflicting results obtained by different workers. The chemical identity of the hydrates was established by electrochemical analysis of the copper content and the crystals were distinguished from one another by their physical properties like colour, stability in air, crystal morphology and optical birefringence.

(b) *Magnetic measurements*

For the measurement of magnetic anisotropy ($\chi_{\parallel}-\chi_{\perp}$) of the hexahydrated crystal a quartz torsion balance was used (Majumdar and Datta, 1965) in the temperature range 300°-90°K. For the susceptibility measurements an improved type of Curie balance (Bose *et al*, 1964) was used for the same temperature range. Measurements were taken at about 20° intervals of temperature. A 'deflection method' was used to study the anisotropy as a continuous function of temperature in the region around the phase transition observed in the crystal (*vide infra*). The crystals are efflorescent around room temperature (which in this country ranges between 25° to 35°C except in winter) and they lose two molecules of water and were, therefore, coated with collodion dissolved in ether immediately after being taken out of the mother liquor.

RESULTS

No measureable anisotropy was observed in the plane normal to the *c*-axis (symmetry axis) in the temperature range studied, as is to be expected, nor was there any visible change of colour, in contrast to similar Co (Majumdar and Datta, 1965) and mixed Co-Mn salts (unpublished) studied earlier which undergo phase changes at low temperatures, although the crystal became very brittle and very often shattered. However, measurements made with the *c*-axis horizontal showed an anomalous minimum in the $T.(\chi_{\parallel}-\chi_{\perp})$ against temperature (T°K) curve around 280°K (figure 1). This was more clearly seen from a measurement of the deflection of the crystal, suspended from a torsion fibre in the magnetic field, as a continuous function of temperature. The minima for the cooling and heating processes were at~285°K and 295°K respectively, exhibiting thermal hysteresis (figure 1, inset). Thus the crystal appears to undergo a phase change at low temperatures. The transition temperatures for the cooling and heating processes were found to be independent of the cooling or heating rates, showing that the hysteresis is real. It is obvious that since we started with the hexahydrate which

is stable below 30°C, the above phase-transition near 10°C cannot be due to the tetrahydrate form which is stable above 30°C.

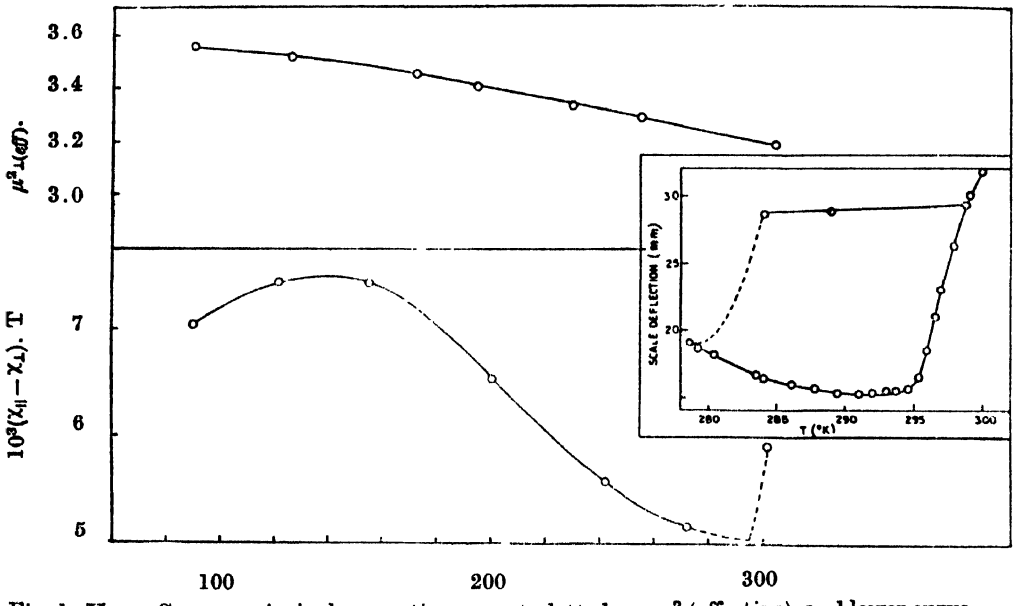

Fig. 1. Upper Curve—principal magnetic moment plotted as $\mu_\perp{}^2$ (effective), and lower curve—magnetic anisotropy plotted as T. $\Delta\chi$, of Cu SiF_6. $6H_2O$ against temperature. Inset: thermal hysterisis in the magnetic anisotropy in the region of phase transition as obtained by the 'deflection method'.

Measurement of the susceptibility was made in the c-plane($i,e.\chi_\perp$). The values of squares of the effective principal moments, $\mu_\perp{}^2$, were obtained from those of $\chi_\perp$ (corrected for diamagnetism) using the relationships $\mu_i{}^2$ (off) $= \frac{3kT}{N\beta^2}\cdot\chi_i = 7.995\chi_i T$. The values for $\chi_\perp$ and $\chi_\parallel - \chi_\perp$ at 20° intervals of temperature were obtained by graphical interpolation from which $\chi_\parallel$ and the mean susceptibility χ were calculated (table 1). It is to be noted that in view of the phase transition the crystal symmetry below the transition temperature may probably be different from trigonal. However, as stated above, the crystal retains its uniaxial magnetic symmetry at low temperatures. In the absence of detailed structural data we assume that there is still one ion in the unit cell at low temperatures, so that the ionic susceptibility K_i is identical with χ_i (i = $\parallel$ or $\perp$). It may also be noted that the anisotropy is very small compared to that of the usual hydrated copper salts, e.g. $CuSO_4$. $5H_2O$, and the Tutton salts (Bose *et al*, 1957). For example, at 300°K, $\chi_\parallel - \chi_\perp$ for the fluosilicate is 20, while in the latter salts $K_\parallel - K_\perp \sim 500$, in the usual 10^{-6} c.g.s.em units. In contrast, the values of the principal susceptibilities (and consequently, their mean value, or the corresponding moments) do not show any noticeable abnormality in the range of temperature studied. Furthermore, the susceptibility values agree well with those of the other hydrated copper salts mentioned above.

Table 1

Magnetic anisotropy and susceptibility of $CuSiF_6.6H_2O$ (from graphical interpolation)

Temp. °K	$10^6 . \chi$	$10^6 (\chi_{\parallel} - \chi_{\perp})$
300	1,338	18.7
280	1,452	18.2
260	1,585	20.4
240	1,739	23.4
220	1,920	27.5
200	2,138	32.7
180	2,406	39.2
160	2,728	46.1
140	3,144	53.6
120	3,689	61.2
100	4,452	71.8
90	4,960	78.1

THEORY

The original free ion electronic configuration of the Cu^{2+} ion being $3d^9$ in this hexahydrated fluosilicate crystal, this may be regarded as a single electron hole in the completed $3d$ subshell subject to a predominant octahedral ligand field arising from the six surrounding water oxygens. Under the octahedral field of symmetry O_h the $3d^9\ ^2D$ ground state of the Cu^{2+} ion splits up into an orbital doublet E_g and a triplet T_{2g} which lies above the doublet. The appropriate cubic field wave functions, using the three-fold axis of the octahedron as the axis of quantization, are (Bleaney and Stevens, 1953) :

Wave functions		*Representation*	
$\sqrt{\frac{2}{3}}\, d_{-2} + \sqrt{\frac{1}{3}}\, d_1$, d_0,	$\sqrt{\frac{2}{3}}\, d_2 - \sqrt{\frac{1}{3}}\, d_{-1}$	T_{2g}	
$\sqrt{\frac{1}{3}}\, d_2 + \sqrt{\frac{2}{3}}\, d_{-1}$,	$\sqrt{\frac{1}{3}}\, d_{-2} - \sqrt{\frac{2}{3}}\, d_1$	E_g	.. (1)

The ligand field potential near the central Cu^{2+} ion is given by

$$G' \left[\frac{1}{20}(35z^4 - 30r^2z^2 + 3r^4) - \sqrt{2}z(x^3 - 3xy^2)\right] + H'(3z^2 - r^2) + I'(35z^4 - 30r^2z^2 + 3r^4) \quad \ldots (2)$$

Following Pryce and Runciman (1958), the appropriate trigonal orbital states are

$$t_0 = +\frac{1}{\sqrt{3}}[(xy)+(yz)+(xz)]$$

$$t_+ = -\frac{1}{\sqrt{3}}[(xy)+\omega(yz)+\omega^2(xz)]$$

$$t_- = +\frac{1}{\sqrt{3}}[(xy)+\omega^{-1}(yz)+\omega^{-2}(xz)] \qquad .. \quad (3)$$

$$e_+ = -\frac{1}{\sqrt{2}}[(z^2)+i(x^2-y^2)]$$

$$e_- = +\frac{1}{\sqrt{2}}[(z^2)-i(x^2-y^2)]\ ;$$

where $\omega = \exp\frac{2\pi i}{3}$

The upper triplet T_{2g} splits up into a singlet and a doublet in the trigonal field of lower symmetry but the doublet E_g remains unsplit even after the application of the trigonal field. According to Jahn and Teller (1937) the electronically degenerate state is unstable (except for the two-fold Kramers degeneracy) with respect to some asymmetric nuclear displacement, which therefore lifts the orbital degeneracy of the said state. In this paper we enumerate only those symmetry coordinates which are of physical interest for our problem. The two-dimensional phase space of the E_g vibration is spanned by the two normal coordinates Q_2 and Q_3, which are described and defined among others, by, Öpik and Pryce (1957) as

$$Q_2(E_g) = \frac{1}{5}[X_1-X_4-Y_2+Y_5]$$

$$Q_3(E_g) = \frac{1}{2\sqrt{3}}[2(Z_2-Z_6)-(X_1-X_4+Y_2-Y_5)] \qquad .. \quad (4)$$

where X_i, Y_i, Z_i represent the x_i, y_i, z_i components, respectively of the displacement of the i-th ligand.

The Hamiltonian of our problem is

$$H_A = H_{el}+H_n+H_{en} \qquad .. \quad (5)$$

in which the first term is the contribution due to the electronic motion, $H_{el} = V_0$; the second term is the contribution from the nuclear vibration. It is given by

$$H_n = H^0{}_n + \tfrac{1}{2}M\omega^2(Q^2{}_2+Q_3{}^2) + A_3Q_3(Q_3{}^2-3Q_2{}^2) \qquad (6)$$

This expression is identical with that derived by Öpik and Pryce (1957) in which $M\omega^2$ and A_3 are parameters with dimensions of energy. M is assumed to be the effective mass of the ligand. The second and the third terms of H_n are classical potential energy expanded in powers of Q to third order. The third term in (6) is the 'anharmonic term' in the 'quasi-elastic' restoring forces. H_{en} is the interaction term arising from the change in the coulombian potential energy as the nuclei composing the complex are displaced. The magnitude of this change for small displacements will be given by the first few terms in the Taylor series expansion, i.e.

$$H_{en} = V^\circ{}_{en} + \left(\frac{\partial V}{\partial Q_2}\right) Q_2 + \left(\frac{\partial V}{\partial Q_3}\right) Q_3 + \tfrac{1}{2}\left(\frac{\partial^2 V}{\partial Q_2{}^2}\right) Q_2{}^2 + \tfrac{1}{2}\left(\frac{\partial^2 V}{\partial Q_3{}^2}\right) Q_3{}^2 + \left(\frac{\partial^2 V}{\partial Q_2 \partial Q_3}\right) Q_2Q_3 + \ldots \qquad (7)$$

Hence we can write the complete Hamiltonian as :

$$H = H_0 + H^{(1)} + H^{(2)} + H' \qquad .. \quad (8)$$

where

$$H_0 \equiv E_0 = V_0 + V_{en}{}^0 + H_n{}^0 + \ldots$$

which is the energy of the complex in the absence of Jahn-Teller distortion;

$$H^{(1)} = \tfrac{1}{2}M\omega^2(Q_2{}^2+Q_3{}^2) + \left(\frac{\partial V}{\partial Q_2}\right) Q_2 + \left(\frac{\partial V}{\partial Q_3}\right) Q_3 \; ;$$

$$H^{(2)} = \tfrac{1}{2}\left(\frac{\partial^2 V}{\partial Q_2{}^2}\right) Q_2{}^2 + \tfrac{1}{2}\left(\frac{\partial^2 V}{\partial Q_3{}^2}\right) Q_3{}^2 + \left(\frac{\partial^2 V}{\partial Q_2 \partial Q_3}\right) Q_2Q_3 + A_3Q_3(Q_3{}^2-3Q_2{}^2) \qquad .. \quad (9)$$

and

$$H' = \frac{1}{2M}(P_2{}^2+P_3{}^2)I$$

where P_2, P_3 are momenta conjugate to Q_2, Q_3 and I is the unit matrix.

At first we ignore the kinetic energy of the nuclei and operate with the Hamiltonian (8) on the trigonal field eigen-functions (3). We obtain

	$\lvert e_+\rangle$	$\lvert e_-\rangle$
$\lvert e_+\rangle$	$\tfrac{1}{2}(V_{aa}+V_{bb})$	$\tfrac{1}{2}(V_{aa}-V_{bb}+2iV_{ab})$
$\lvert e_-\rangle$	$\tfrac{1}{2}(V_{aa}-V_{bb}-2iV_{ab})$	$\tfrac{1}{2}(V_{aa}+V_{bb})$

.. (10)

$$\begin{array}{lccc} & |t_+> & |t_-> & |t_0> \\ |t_+> & 10Dq+\frac{1}{5}\Delta & 0 & |t_0> \quad 10Dq-\frac{2}{5}\Delta \\ |t_-> & 0 & 10Dq+\frac{1}{5}\Delta & \end{array} \quad .. \quad (11)$$

where $10Dq$ is the magnitude of the splitting of the d-orbitals in an octahedral field; $10Dq = 2/7G'\bar{r}^4e$ and Δ is the trigonal field parameter which can be expressed as a linear combination of the trigonal field coefficients H' and I' as

$$\Delta = \frac{4}{7}(H'\bar{r}^2+6I'\bar{r}^4)$$

$$V_{aa} = <d_{x^2-y^2}|H^{(1)}+H^{(2)}|d_{x^2-y^2}>$$

$$= \frac{1}{2}M\omega^2(Q_2^2+Q_3^2)+\left(\frac{\partial V_a}{\partial Q_3}\right)Q_3+\frac{1}{2}\left(\frac{\partial^2 V_a}{\partial Q_3^2}\right)Q_3^2+\frac{1}{2}\left(\frac{\partial^2 V_a}{\partial Q_2^2}\right)Q_2^2+A_3Q_3(Q_3^2-3Q_2^2);$$

$$V_{bb} = <d_{z^2}|H^{(1)}+H^{(2)}|d_{z^2}>$$

$$= \frac{1}{2}M\omega^2(Q_2^2+Q_3^2)+\left(\frac{\partial V_b}{\partial Q_3}\right)Q_3+\frac{1}{2}\left(\frac{\partial^2 V_b}{\partial Q_3^2}\right)Q_3^2+\frac{1}{2}\left(\frac{\partial^2 V_b}{\partial Q_2^2}\right)Q_2^2$$

$$+A_3Q_3(Q_3^2-3Q_2^2); \quad .. \quad (12)$$

$$V_{ab} = <d_{x^2-y^2}|H^{(1)}+H^{(2)}|d_{z^2}>$$

$$= \left(\frac{\partial V_{ab}}{\partial Q_2}\right)Q_2+\left(\frac{\partial^2 V_{ab}}{\partial Q_2 \partial Q_3}\right)Q_2Q_3;$$

Also we have the following relations between the derivatives involved

$$\left.\begin{array}{l} \left(\frac{\partial V_a}{\partial Q_3}\right) = \left(\frac{\partial V_{ab}}{\partial Q_2}\right) = -\left(\frac{\partial V_b}{\partial Q_3}\right); \\ \left(\frac{\partial^2 V_a}{\partial Q_3^2}\right) = \left(\frac{\partial^2 V_b}{\partial Q_2^2}\right); \left(\frac{\partial^2 V_a}{\partial Q_2^2}\right) = \left(\frac{\partial^2 V_b}{\partial Q_3^2}\right); \\ \frac{1}{2}\left(\frac{\partial^2 V_a}{\partial Q_3^2}\right) - \left(\frac{\partial^2 V_a}{\partial Q_2^2}\right) = -\left(\frac{\partial^2 V_{ab}}{\partial Q_2 \partial Q_3}\right) \end{array}\right\} \quad .. \quad (13)$$

In the construction of the above secular determinants we have operated only with the first term in (8) on the upper T_{2g} state as the Jahn-Teller coupling of the E_g state with the lattice vibrations will be at least several times as strong as that of the T_{2g} state which we may assume to be undistorted (O'Brien, 1965; Jones 1967). The problem is thus similar to that considered by Longuet-Higgins *et al* (1958) who considered the coupling of an E_g electronic state to the E_g modes of vibration of an octahedron of neighbours.

To evaluate the eigenfunctions and eigenvalues of the secular determinant (10) we proceed to first order $H = H^{(1)}$ and take $H_0 = E_0$, the energy of the degenerate state in the symmetrical configuration as zero reference, when we obtain

$$\begin{pmatrix} \frac{1}{2}M\omega^2(Q_2^2+Q_3^2) & g\omega(Q_3+iQ_2) \\ g\omega(Q_3-iQ_2) & \frac{1}{2}M\omega^2(Q_2^2+Q_3^2) \end{pmatrix} \quad .. \quad (14)$$

which gives

$$E = \tfrac{1}{2}M\omega^2(Q_2^2+Q_3^2) \pm g\omega(Q_2^2+Q_3^2)^{\frac{1}{2}} \quad .. \quad (15)$$

where $$g\omega = \left(\frac{\partial V_a}{\partial Q_3}\right)$$

To solve the above equation we define polar coordinates ρ and θ in the space of the coordinates Q_2 and Q_3 :

$$Q_2 = \rho \sin\theta; \qquad Q_3 = \rho\cos\theta \quad .. \quad (16)$$

which gives

$$E = \tfrac{1}{2}M\omega^2\rho^2 \pm g\omega\rho$$

The minimum value of energy can be easily found from above, as

$$E_{min} = -g^2/2M; \qquad \Delta E_g = 2g\omega\rho_0$$

where $$\rho_0 = (Q_2^2+Q_3^2)^{\frac{1}{2}} = g/\omega M. \quad .. \quad (17)$$

Therefore, to the first order the energy stabilization is independent of θ, which implies that there is no static distortion of the complex, but a dynamic resonance between the modes Q_2 and Q_3 in which the electronic configuration remains in phase with the modes of nuclear vibration.

To the second order, $H = H^{(1)}+H^{(2)}$, and we obtain from (10)

$$\begin{pmatrix} \frac{1}{2}M\omega^2(Q_2^2+Q_3^2)+\delta(Q_2^2+Q_3^2)+A_3(Q_3^2-3Q_2^2)Q_3 & \\ g\omega(Q_3-iQ_2)+\beta(Q_3^2-Q_2^2)+i\beta Q_2Q_3 & \\ & g\omega(Q_3+iQ_2)+\beta(Q_3^2-Q_2^2)-i\beta Q_2Q_3 \\ & \frac{1}{2}M\omega^2(Q_2^2+Q_3^2)+\delta(Q_2^2+Q_3^2)+A_3(Q_3^2-3Q_2^2)Q_3 \end{pmatrix} \quad ... \quad (18)$$

in which the various symbols used are as follows:

$$\delta = \frac{1}{4}\left(\frac{\partial^2 V_a}{\partial Q_3^2} + \frac{\partial^2 V_a}{\partial Q_2^2}\right)$$

$$2\alpha = \frac{1}{2}\left(\frac{\partial_2 V_a}{\partial Q_3^2} - \frac{\partial^2 V_a}{\partial Q_2^2}\right) = -\left(\frac{\partial^2 V_{ab}}{\partial Q_2 \partial Q_3}\right)$$

Thus if the kinetic energy of the nuclei is ignored, the electronic eigenstates corresponding to the E_g level take the form

$$\sin \tfrac{1}{2}\theta\,|e_+> - \cos \tfrac{1}{2}\theta\,|e_-> ; \quad \cos \tfrac{1}{2}\theta\,|e_+> + \sin \tfrac{1}{2}\theta\,|e_-> \qquad .. \quad (19)$$

where $\alpha \approx 0$

The corresponding eigenvalues are given by

$$E = \tfrac{1}{2}(M\omega^2+\delta)\rho_0^2 + A_3\rho_0^3 \cos 3\theta \pm g\omega\rho_0 \qquad .. \quad (20)$$

From this we get the energy of the system to be minimum,

$$E_1 = \tfrac{1}{2}(M\omega^2+\delta)\rho_0'^2 + A_3\rho_0'^3 - g\omega\rho_0'; \; \Delta E_g = 2g\omega\rho_0'$$

where $$\rho_0' = \frac{(M\omega^2+\delta) - [(M\omega^2+\delta) - 12g\omega\,|A_3|\,]^{\frac{1}{2}}}{6\,|A_3|} \qquad .. \quad (21)$$

where E_1 is the energy eigenvalue corresponding to the ground state and ΔE_g is the magnitude of the Jahn-Teller shift of the orbital E_g doublet.

The vibronic eigenfunctions ψ being the products of one of the electronic functions and the harmonic oscillator wave functions (Moffitt and Thorson, 1957) are given by

$$\left.\begin{aligned} \psi_1 &= \sin \tfrac{1}{2}\theta'\,|e_+> - \cos \tfrac{1}{2}\theta'\,|e_-> ; \\ \psi_2 &= \cos \tfrac{1}{2}\theta'\,|e_+> + \sin \tfrac{1}{2}\theta'\,|e_-> ; \\ \psi_3 &= |t_0> ; \quad \psi_4 = |t_-> ; \qquad \psi_5 = |t_+> ; \end{aligned}\right\} \qquad \ldots \quad (22)$$

and the corresponding eigenvalues are

$$\left.\begin{aligned} E_1 &= \tfrac{1}{2}(M\omega^2+M+\delta)\rho_0'^2 + A_3\rho_0'^3 - g\omega\rho_0' ; \quad \Delta E_g = 2g\omega\rho_0' ; \\ E_3 &= 10Dq - \tfrac{2}{5}\Delta ; \\ E_4 &= 10Dq + \tfrac{1}{5}\Delta ; \end{aligned}\right\} \qquad \ldots \quad (23)$$

where θ' may be conveniently taken as the product of θ in the electronic wave function and some function of θ which appears in the harmonic oscillator wave functions. Since a change in ρ does not alter the electronic state, only the contribution to the nuclear kinetic energy from changes in θ has been considered (O' Brien, 1964).

Calculation of g-values

In calculating g-values and the magnetic susceptibilities we adopt Pryce's (1950) spin-Hamiltonian formalism. The spin-Hamiltonian is given by

$$H_s = \langle\psi_1|H'|\psi_1\rangle - \sum_{n\neq 1} \frac{\langle\psi_1|H'|\psi_n\rangle\langle\psi_n|H'|\psi_1\rangle}{E_n - E_1}$$

$$+ \sum_{m\neq 1}\sum_{n\neq 1} \frac{\langle\psi_1|H'|\psi_m\rangle\langle\psi_m|H'|\psi_n\rangle\langle\psi_n|H'|\psi_1\rangle}{(E_m-E_1)(E_n-E_1)}$$

$$- \sum_{n\neq 1} \frac{\langle\psi_1|H'|\psi_n\rangle\langle\psi_n|H'|\psi_1\rangle\langle\psi_1|H'|\psi_1\rangle}{(E_n-E_1)^2} \quad .. \quad (24)$$

where H' stands for the perturbation Hamiltonian and is given by

$$H' = \lambda \boldsymbol{LS} + \beta \boldsymbol{H}(\boldsymbol{L}+2\boldsymbol{S}),$$

in which λ is the spin-orbit coupling parameter for the free ion.

Before applying the spin-Hamiltonian we transform the z-axis along the (111) direction as in our construction of the wave functions (3) we have considered the z-axis along the fourfold symmetry axis. For this we apply the following unitary transformation

$$\begin{pmatrix} L_\xi \\ L_\eta \\ L_\zeta \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} & 0 \\ \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & -\sqrt{\frac{2}{3}} \\ \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} \quad .. \quad (26)$$

For $H//\zeta$-axis, we obtain the spin-Hamiltonian (Bose *et al*, 1965)

$$H_s(\zeta) = 2\beta H S_\zeta - \Big[\Big\{ \frac{4\lambda R_\zeta \kappa_\zeta S_\zeta}{\Delta_{41}} + \frac{2\sqrt{2} i a_1 b_1 \lambda R_\xi (S_- - S_+)}{\Delta_{41}} \Big\} \beta H + \frac{2\kappa_\zeta{}^2 \beta^2 H^2}{\Delta_{41}} \Big] \quad .. \quad (27)$$

Similarly, the spin-Hamiltonian along ξ-axis is

$$H_s(\xi) = 2\beta H S_\xi - \Big[\Big(\frac{1+2a_1b_1}{\Delta_{31}} + \frac{1}{\Delta_{41}} \Big) \lambda R_\xi \kappa_\xi (S_+ + S_-)\beta H + \Big(\frac{1+2a_1b_1}{\Delta_{31}} + \frac{1}{\Delta_{41}} \Big) \kappa_\xi{}^2 \beta^2 H^2 \Big] \quad (28)$$

and along η-axis, it is

$$H_s(\eta) = 2\beta H S_\eta - \Big[\Big\{ \frac{i(1-2a_1b_1)(S_- - S_+)\lambda R_\eta \kappa_\eta}{\Delta_{21}}$$

$$+\frac{4\sqrt{2}a_1b_1\lambda R_\zeta \kappa_\eta S_\zeta + i(S_- - S_+)\lambda R_\eta \kappa_\eta}{\Delta_{41}}\Big\} \beta H$$

$$+\left(\frac{1-2a_1b_1}{\Delta_{31}}+\frac{1}{\Delta_{41}}\right)\kappa_\eta{}^2\beta^2H^2\Big] \quad .. \quad (29)$$

where we have symbolized the separation $E_m - E_n$ as Δ_{mn}, $a_1 = \sin\frac{1}{2}\theta'$, $b_1 = \cos\frac{1}{2}\theta'$ and κ_i's and R_i's are known as the orbital reduction and spin-orbit coupling reduction factors, respectively, arising from the covalency effects. Following Owen (1955), Stevens (1953) and others, to avoid computational difficulties, we take κ_i and R_i to be isotropic and roughly of the same order of magnitude. This does not matter very much since the overlaps are themselves small and contribute only a small part to the anisotropy in g_i which is itself a very small quantity in the copper fluosilicates. In equations (27-29) terms independent of H have been omitted since they do not produce any zero-field splitting of the Kramers' degenerate spin-states $|\pm\frac{1}{2}>$ in the absence of the magnetic field. The terms involving β^2H^2 also do not produce any splitting of the degenerate components and are not important in the calculation of g-values, but are quite appreciable in the calculation of susceptibilities, contributing to the temperature-independent paramagnetism and hence are retained. As the first excited state $|\psi_2>$ is presumably not much higher in energy compared to kT at room temperatures this state is also populated appreciably at ordinary temperatures. Hence, we apply the perturbation Hamiltonian upon the states $|\psi_1>$ and $|\psi_2>$. Since, the state $|\psi_2>$ is not coupled to the ground state $|\psi_1>$ by the spin-orbit coupling we may treat the two levels separately and use the spin-Hamiltonian formalism.

At first we consider the field applied parallel to ζ-axis. Operating the Hamiltonian $H_s(\zeta)$ on the spin-states $|\pm\frac{1}{2}>$ we get a secular matrix which on diagonalization gives the following energy-values :

$$W_i(\zeta) = \pm\tfrac{1}{2}\sum_{i=1,2} g^i(\zeta)\beta H - 2\left(\frac{1}{\Delta_{41}}+\frac{1}{\Delta_{42}}\right)\beta^2H^2\kappa^2 \quad .. \quad (30)$$

where $$g^i(\zeta) = 2\left[\left(1-\frac{2\lambda R\kappa}{\Delta_{4i}}\right)^2+\left(\frac{2\sqrt{2}a_1b_1\lambda R\kappa}{\Delta_{4i}}\right)^2\right]^{\frac{1}{2}} \quad .. \quad (31)$$

For $H//\eta$-axis

$$W_i(\eta) = \pm\tfrac{1}{2}\sum_{i=1,2} g^i(\eta)\beta H - \left[\frac{1-2a_1b_1}{\Delta_{31}}+\frac{1+2a_1b_1}{\Delta_{32}}+\left(\frac{1}{\Delta_{41}}+\frac{1}{\Delta_{42}}\right)\right]\beta^2H^2\kappa^2$$

where $$g^i(\eta) = 2\left[\left(\frac{2\sqrt{2}a_1b_1\lambda R\kappa}{\Delta_{4i}}\right)^2+\left\{1-\frac{\lambda RK(\mp 2a_1b_1)}{\Delta_{3i}}-\frac{\lambda R\kappa}{\Delta_{4i}}\right\}^2\right]^{\frac{1}{2}} \quad .. \quad (33)$$

and for $H//\xi$-axis

$$W_i(\xi) = \pm \tfrac{1}{2} \sum_{i=1,2} g^i(\xi)\beta H - \Big[\frac{1+2a_1b_1}{\Delta_{31}} + \frac{1-2a_1b_1}{\Delta_{32}} + \Big(\frac{1}{\Delta_{41}} + \frac{1}{\Delta_{42}} \Big) \Big] \beta^2 H^2 \kappa^2 \quad \ldots (34)$$

where,

$$g^i(\xi) = 2\Big[1 - \frac{(1\pm 2a_1b_1)\lambda R\kappa}{\Delta_{3i}} - \frac{\lambda R\kappa}{\Delta_{4i}}\Big] \quad \ldots (35)$$

$(i = 1, 2)$

(the upper and the lower signs (+or −) in the expressions (33) and (35) are for $i = 1$ and 2, respectively).

Liehr and Ballhausen (1958) and others have shown that the configuration $Cu^{2+}(H_2O)_6$ cluster undergoes a static distortion at low temperatures where θ' assumes a definite value and becomes non-cyclic due to trapping by the minima. In that case, the g-values are given by (31), (33) and (35). The g-values can be fitted to experiment by taking $\theta' = j\pi/3$; $(j = 0, 2, 4)$. But at higher temperatures (above 60°K) the vibrational motions could be considered as cyclic in θ' which gives $a_1b_1 = 0$ in (31), (33) and (35).The g-values are then to be averaged over θ' and are given by

$$g_{\|}{}^i = g^i(\zeta) = 2(1 - \lambda RK\alpha_{\|}{}^i); \quad \ldots (26)$$

$$g_{\perp}{}^i = g^i(\xi) = g^i(\eta) = 2(1 - \lambda RK\alpha_{\perp}{}^i);$$

where $\alpha_{\|}{}^i = 2/\Delta_{4i}$;

and $\alpha_{\perp}{}^i = \Big(\frac{1}{\Delta_{3i}} + \frac{1}{\Delta_{4i}} \Big)$; $(i = 1, 2)$.

In the above perturbation calculation we have considered up to second-order terms in the case of E_1 and E_2 as the contribution from the third order terms are negligibly small.

CALCULATION OF SUSCEPTIBILITIES

The expression for the principal gm-ionic magnetic susceptibility is given as usual by

$$K_i = \underset{H\to 0}{\text{Lt.}} - \frac{N}{H} \cdot \frac{\sum_s \frac{\partial W_s^{(i)}}{\partial H} \exp(-W_s^{(i)}/kT)}{\sum_s \exp(-W_s^{(i)}/kT)} \quad (38)$$

On substituting the values of $W_s^{(i)}$ from (30), (32) and (34) in the above expression, we obtain

$$K_{\parallel} = \frac{2N\beta^2}{k}\left[k\kappa\left\{\frac{\alpha_{\parallel}^{(1)}}{1+\exp\left(-\frac{\Delta E_g}{kT}\right)}+\frac{\alpha_{\parallel}^{(2)}}{1+\exp\left(\frac{\Delta E_g}{kT}\right)}\right\}\right.$$

$$\left.+\frac{1}{8T}\left\{\frac{g_{\parallel}^{(1)^2}}{1+\exp\left(-\frac{\Delta E_g}{kT}\right)}+\frac{g_{\parallel}^{(2)^2}}{1+\exp\left(\frac{\Delta E_g}{kT}\right)}\right\}\right]$$

and

$$K_{\perp} = \frac{2N\beta^2}{k}\left[kK\left\{\frac{\alpha_{\perp}^{(1)}}{1+\exp\left(-\frac{\Delta E_g}{kT}\right)}+\frac{\alpha_{\perp}^{(2)}}{1+\exp\left(\frac{\Delta E_g}{kT}\right)}\right\}\right.$$

$$\left.+\frac{1}{8T}\left\{\frac{g_{\perp}^{(1)2}}{1+\exp\left(-\frac{\Delta E_g}{kT}\right)}+\frac{g_{\perp}^{(2)2}}{1+\exp\left(\frac{\Delta E_g}{kT}\right)}\right\}\right] \quad \ldots (39)$$

where ΔE_g is given by the equation (21), whence we have themean susceptibility

$$\bar{K} = \tfrac{1}{3}(K_{\parallel}+2K_{\perp})$$

and anisotropy,

$$\Delta K = (K_{\parallel}-K_{\perp}) \quad \ldots (40)$$

DISCUSSIONS

Expressions (36), (39) and (40) are now used to fit the experimental results on e.s.r. g-values, magnetic anisotropy and mean susceptibility in the range of temperatures 300°K to 90°K. For this purpose we have taken the magnetic anisotropy and susceptibility measurements by Majumdar (1966) in the temperature range 300°K to 90°K, the g-values at 90°K for $CuSiF_6.6H_20$ diluted with the isomorphous zinc salt by Bleaney and Ingram (1950) and at 300°K the g-value is for the undiluted salt by Yokozawa (1954). The number of theoretical parameters appearing in the expressions for the e.s.r. g-values, magnetic susceptibilities and the energy-values of the ligand field levels in the optical spectra are : the cubic field splitting parameter $10Dq$, the trigonal field parameter Δ, the Jahn-Teller splitting parameter ΔE_g, the mean orbital reduction and the mean spin-orbit coupling reduction factors κ and R. The cubic field parameter $10Dq$ was estimated from the available optical absorption data (Griffith, 1961) which show a broad peak around 12,600 cm^{-1}. Having fixed the value of the parameter $10Dq$, the remaining three parameters, viz. Δ, ΔE_g and κ ($= R$) were then adjusted by

trial so as to fit the experimental results on susceptibility, anisotropy and the g-values as well as possible, taking the values at 90°K to be the standard.

Table 2

Values of the parameters showing the closest fit between the theoretical and experimental results on $CuSiF_6.6H_2O$

$10Dq = 12{,}700\ cm^{-1}$ $\quad \kappa = R = 0.85$

$\Delta E_g = -400\ cm^{-1}$ $\quad \lambda = -829\ cm^{-1}$ (free ion value)

Susceptibilities

Temp °K	$10.^4\alpha_{\|\|}$	$10.^4\alpha_\perp$	$10^6.K$	$10^6.\Delta K$
300	$\alpha_{\|\|}^{(1)}=0.75$ $\alpha_{\|\|}^{(2)}=0.56$	$\alpha_\perp^{(1)}=0.60$ $\alpha_\perp^{(2)}=0.47$	1344 (1338)	19 (18.7)
260	$\alpha_{\|\|}^{(1)}=0.85$ $\alpha_{\|\|}^{(2)}=0.75$	$\alpha_\perp^{(1)}=0.75$ $\alpha_\perp^{(2)}=0.67$	1592 (1585)	20.1 (20.4)
200	$\alpha_{\|\|}^{(1)}=1.13$ $\alpha_{\|\|}^{(2)}=1.04$	$\alpha_\perp^{(1)}=1.06$ $\alpha_\perp^{(2)}=0.92$	2135 (2138)	33 (32.7)
140	$\alpha_{\|\|}^{(1)}=1.40$ $\alpha_{\|\|}^{(2)}=1.35$	$\alpha_\perp^{(1)}=1.35$ $\alpha_\perp^{(2)}=1.20$	3146 (3144)	54 (53.6)
90	$\alpha_{\|\|}^{(1)}=1.54$ $\alpha_{\|\|}^{(2)}=1.50$	$\alpha_\perp^{(1)}=1.41$ $\alpha_\perp^{(2)}=1.37$	4955 (4960)	77.8 (78.1)

g-values

Theoretical		Experimental	
at 300°K	at 90°K	at 300°K	at 90°K
$g_{\|\|}^{(1)}=2.11$	$g_{\|\|}^{(1)}=2.19$		
$g_{\|\|}^{(2)}=2.10$	$g_{\|\|}^{(2)}=2.18$	$g_{\|\|}=g_\perp=2.2$ (Yokozawa, 1954)	$g_{\|\|}=g_\perp=2.24$ (Bleaney & Ingram 1950)
$g_{\|\|}^{(1)}=2.10$	$g_\perp^{(1)}=2.18$		
$g_{\|\|}^{(2)}=2.09$	$g_\perp^{(2)}=2.17$		

(The experimental g-values at 90°K obviously refer to the lower level E_1 of the orbital doublet as the e.s.r. signal from the upper E_2 level may be too weak to observe).

It is to be noted that the values of α_i's have been so chosen as to give a good fit with the experimental anisotropy values. $\alpha_{\|\|}$'s have thus been found to be greater than $\alpha_\perp$'s in our case, assuming of course that the orbital and spin-orbit reduction factors to be isotropic. Correlating the α's with the lower symmetric field parameter Δ it is easy to see that $\alpha_{\|\|}$ is to be greater than $\alpha_\perp$, which would make Δ negative as the sign of the parameter Δ depends upon $\alpha_{\|\|}$ and $\alpha_\perp$ (eqn. 37).

Öpik and Pryce (1957) have pointed out that for $Cu^{2+}(H_2O)_6$ A_3 is negative, which would make ΔE_g also negative (eqn. 21). Changing the sign of ΔE_g would interchange the values of $\alpha_i^{(1)}$ and $\alpha_i^{(2)}$, although an inspection of equation (39) shows that the anisotropy and susceptibility values would still remain unchanged. However, following Öpik and Pryce we have considered ΔE_g as a negative quantity. The magnitude of ΔE_g may not be a true estimate of the Jahn-Teller splitting because we have neglected the effect of charges beyond the nearest neighbours surrounding the Cu^{2+} ion in our calculations. Such effect may be comparable to the Jahn—Teller effect (Van Vleck, 1939) and may materially affect the value of ΔE_g.

In fitting the experimental results for different temperatures κ, R and Dq are assumed to remain invariant with temperature. The parameters that are most likely to vary are the α_i's which are directly related to the energy separations E_4-E_i, E_3-E_i ($i = 1$ and 2), (Eqn. 37). Now E_3 and E_4 are functions of Dq and Δ, while E_i's involve normal coordinates Q_2, Q_3 besides the other parameter, viz. the effective mass of the ligand which may reasonably be assumed to be temperature independent. Till now no experimental data in our temperature range are available; we, therefore, have not considered *separately* the thermal variation of these vibrational parameters in our work.

The parameters best suited to fit the theory with the experimental results are shown in table 2. The results indicate that the value of the reduction factors $\kappa = R = 0.85$ gives reasonable fit. Thus the orbital moment and the spin-orbit coupling coefficient are both reduced by 15 per cent, due to covalency effect, from the free ion value.

The discrepancy between the calculated and experimental g-values for 300°K may arise because of the fact that parametral fittings were carried out to fit the g-values at 90°K which are for the diluted salt (Bleaney and Ingram, 1950),whereas the g-value at 300°K has been experimentally observed by Yokozawa (1954) on an undiluted salt and there may be some difference in the g-values of the two systems. It may also be noted that previous workers based their calculations on purely octahedral model which accounts for the fact, that at low temperatures when "trapping" occurs, the set of three ions having anisotropic g-values are directed along the "principal cube edges" (Abragam and Pryce, 1950). This would result in isotropic g-values as well as susceptibility in our temperature range (neglecting contribution from the high frequency terms). However, we have here taken into consideration the lower symmetry field so that the slight anisotropy in g arises naturally. The occurrence of the phase transition in this crystal may, perhaps, be related to the transition from dynamic to static Jahn-Teller distortion. The theory of the thermal stability of the crystal lattice under such distortions is being investigated.

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